can be formed in the same way as for the white, but it entails not only a black disc in the outer ring, but also a white disc, for the mixed colours in the inner discs contain as a rule more white than does the yellow. It was my intention to have mentioned in this communication the question of the colours which the incompletely colour-blind see, or say they see, but, as the foregoing results are based on measures of colours and not on the colours themselves, I have reserved this subject for possibly another communication.

A Chemically Active Modification of Nitrogen produced by the Electric Discharge.—II.*

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1. *Behaviour with Oxygen and Hydrogen.*

It was noticed previously[†] that oxygen destroyed the nitrogen afterglow. There is no doubt whatever that this is a positively destructive effect, as opposed to a mere dilution. For if a stream of oxygen is admitted through a stopcock into the stream of glowing nitrogen, the glow is extinguished: replacing the oxygen with an equal (inert) nitrogen feed, the nitrogen glow reappears, only slightly weakened by dilution.

No oxidation of nitrogen accompanies the destruction of the glow. The mixed gases were passed through a U-tube cooled in liquid air for half-an-hour. No deposit could be seen in the tube. The condensed gases from the U-tube (if any) were collected through a Töpler pump on warming up. Nothing was collected beyond about $\frac{1}{2}$ c.c. of nitrogen, which was presumably derived from leakage, since liquid air could not have condensed it.

Any oxide of nitrogen except nitric oxide would be completely collected in the cooled tube. Nitric oxide, if it had been formed, would have been further acted on by the active nitrogen, forming nitrogen peroxide, which would have been at once detected.[‡] It can only be concluded that the destruction of active nitrogen by oxygen is catalytic, and analogous to its

destruction by cupric oxide.*   These experiments seem to prove that active nitrogen plays no part in the oxidation of nitrogen by the electric spark, as for instance in preparing argon.

Hydrogen, so far as the luminous phenomena are concerned, merely dilutes the active nitrogen, without exhibiting its own spectrum.†   The issuing gases are neutral to litmus paper, there is therefore no formation of ammonia, and in all probability no chemical action at all.

2. *Reaction with Nitric Oxide.*

Nitric oxide led into active nitrogen combines with it, giving rise to a greenish-yellow flame with continuous spectrum, and forming nitrogen peroxide.‡   At the time when the former paper was written, it had unaccountably escaped me that this flame is *identical with that observed when nitric oxide unites with ozone* (the air afterglow).§   Evidence of this from the spectroscopic side is of necessity not very cogent, but the continuous spectra of the two have the same range of wave-lengths.   When, however, the flames are produced side by side for comparison, the peculiar tint is seen identically in each, so as to satisfy the mind completely.

The same flame is developed, though less conspicuously, when nitrogen peroxide is led into the active nitrogen.   The nitrogen peroxide used was prepared by heating lead nitrate, and purified by liquid air condensation. Conditions under which I have observed this flame may be summarised thus—

(1) Ozone mixed with nitric oxide.
(2) Ozone mixed with nitrogen peroxide.
(3) Active nitrogen mixed with nitric oxide.
(4) Active nitrogen mixed with nitrogen peroxide.
(5) Nitric oxide fed into Bunsen flame.
(6) Nitrogen peroxide fed into Bunsen flame.

If the yellowish-green luminosity is regarded as due to the vibration of some particular atomic or molecular system, it seems likely that this system is the nitrogen peroxide molecule.

In cases (2) and (4) nitric oxide is certainly absent, whereas in all cases nitrogen peroxide is present, either originally or as the product of a reaction.

In cases (1) and (2) nitrogen pentoxide is formed.   But in (3) and (4) it is absent, the product of reaction being the peroxide.

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* *Loc. cit.*, p. 226.
† Helium fed into the glowing nitrogen behaves similarly.
‡ *Loc. cit.*, p. 227.
§ 'Phys. Soc. Proc.,' Dec. 15, 1911, vol. 23, p. 66.

Assuming that the greenish-yellow glow is due to the nitrogen peroxide molecule, it must be supposed that in case (4) it is merely stimulated by the energy of the active nitrogen, without chemical change. In the other cases, chemical action occurs and may assist the stimulation. This is quite parallel to what happens in the case of cyanogen.*

The reaction with nitric oxide has been made use of to estimate the percentage of active nitrogen in the total nitrogen leaving an electric discharge. The method was to add excess of nitric oxide to the glowing nitrogen, and to weigh the resulting blue substance which is condensed out from the gases by liquid air.

The blue substance is regarded as nitrogen trioxide, N_2O_3. It is formed by two successive reactions. The first of these results in the formation of nitrogen peroxide,

$$2NO + N = NO_2 + N_2.$$
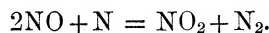
Nitrogen peroxide then combines (at a low temperature) with more nitric oxide, to form the blue substance,

$$NO_2 + NO = N_2O_3.$$
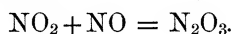
Thus 14 parts by weight of active nitrogen yield 76 parts of the blue substance. The reaction is therefore very advantageous in respect of the large mass of the product.

The N_2O_3 was weighed in a **U**-tube provided with glass stopcocks. It was found that some excess of NO was apt to be condensed, in solution or otherwise, along with the N_2O_3. To get rid of this the **U**-tube was allowed to warm up to about $-50°$ C. and the NO pumped off. No sensible evaporation of N_2O_3 occurs at this temperature. The tube was then closed, and weighed at the ordinary temperature.

In a typical experiment, 540 c.c. of nitrogen were passed through a vacuum tube and then mixed with nitric oxide. The total volume of the latter passed was 460 c.c. It was, therefore, present in ample excess. The weight of N_2O_3 collected was 90 mgrm.

Thus the percentage of nitrogen converted to the active form was 2·46. Other determinations gave similar results.

This is a much higher value than the 0·5 per cent. obtained in my former experiments, in which active nitrogen was determined by phosphorus absorption.† The conditions cannot be kept very constant, but the inevitable variations will not explain this great difference. Nor is it easily explained by any different view of the chemical changes involved. I am inclined to

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* *Loc. cit.*, pp. 226, 228.
† *Loc. cit.*, p. 223.

attribute it to an action of phosphorus in destroying active nitrogen, similar to that of oxygen as described above. On this view, active nitrogen, on coming into contact with phosphorus or its vapour, in part combines and is in part destroyed without combination. The former portion alone is estimated, and the result is necessarily low.

3. *Action on Phosphorus.*

In this connection some very peculiar phenomena may be recorded, of which, however, I can offer no satisfactory interpretation. For the Royal Society Soirée in May last a large vessel was prepared, into which a jet of glowing nitrogen was delivered from a vacuum tube. A large power air pump maintained the vacuum. The vessel filled up in a few seconds with glowing nitrogen, giving a magnificent orange light. If the discharge was turned off this luminosity faded away, partly owing to its natural decay and partly to replacement with non-excited nitrogen entering the vessel. Frequently, however, the following effect was noticed: About 1½ or 2 seconds after the discharge was turned off a new luminosity was seen entering the vessel from the jet, much whiter in colour, and giving a continuous spectrum. This expanded, nearly filling the vessel, and then died down to nothing. Its duration may have been about 2 seconds. There was a well-marked dark cone about the jet, showing clearly that the luminosity was due to some reaction between the gas already present, which had been subjected to the discharge, and that entering at the time, which had not.

After some trouble, the proximate cause of this effect was found to be as follows: The nitrogen stream had been purified from residual oxygen by passing through a tube filled with chips of phosphorus, and thus carried phosphorus vapour with it into the vacuum tube. While the current is passing, this phosphorus at once combines with nitrogen in the discharge tube, and none of it enters the large vessel. When the discharge stops, phosphorus vapour comes through and reacts with the active nitrogen remaining in the large vessel. The reaction produces the mysterious jet of whitish luminosity; but the difficulty remains, why does not this action occur at once instead of hanging fire until the nitrogen in the large vessel has nearly lost its orange glow, and therewith (as all the other phenomena had led one to suppose) its active properties?

This " hang fire " may be better examined by the following modification of the experiment, which admits of continuous observation :—

The experimental tube is as shown. The nitrogen glow dies out about the point A. An independent jet of nitrogen, saturated with phosphorus vapour, but not activated, enters through the jet B into the glow. As soon

as this jet is turned on, a flame with a continuous spectrum appears at C, separated by a considerable dark interval, not only from the jet, but from the boundary of the nitrogen glow.

If the jet B is pushed forward to the point C, the flame burns at its
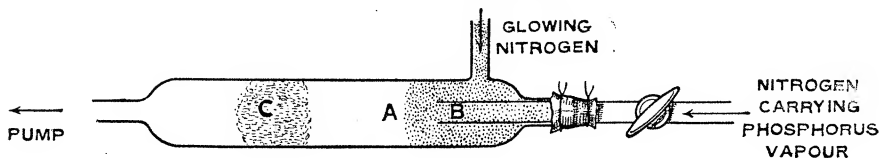
mouth, and continues to do so even if it is pushed considerably further, though in this latter case the intensity is progressively diminished.

The experiment seems to prove that after activated nitrogen has completely undergone the change which gives rise to the glow, some second change must occur before it is prepared to combine with phosphorus vapour. Thus the phenomena are complicated, and it seems doubtful if the current atomic or molecular conceptions of chemistry will suffice to describe them.

4. *Electrical Properties of Glowing Nitrogen.*

Glowing nitrogen is found to possess very marked electrical conductivity. If two electrodes are immersed in it, it is found that a current able to produce a large deflection on an ordinary high resistance galvanometer can be sent between them by a single battery cell. Without attempting elaborate quantitative statements, it may be said generally that the conductivity is of the same order as in a salted Bunsen flame.

The question now presses for answer: Where do the ions thus present in the glowing nitrogen originate? Do they come from the original discharge, or are they generated afterwards, in the course of the changes occurring in the glowing nitrogen?

In the first place, it is to be noted that no conductivity of this order can be observed in the issuing gases when air* or oxygen or hydrogen is substituted for nitrogen. There is, indeed, ionisation surviving from the discharge, but though conspicuous to electrostatic methods of measurement, it falls far short of what can be observed on an ordinary galvanometer. Large conductivity is peculiar to nitrogen pure enough to give the afterglow. Moreover, the testing electrodes must be immersed in the glowing gas. If they are situated beyond the termination of the glow, the galvanometer is not deflected.

These observations decidedly suggest that the large formation of ions

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* The air afterglow does not appear to give rise to any measurable ionisation, even when very conspicuously developed.

occurs in the afterglow, and that they are not derived straight from the original discharge. But the following experiment seems conclusive. Oxygen destroys the afterglow (see above, § 1). Now we cannot suppose that the introduction of oxygen would destroy a pre-existing ionisation in the nitrogen. Yet it is found that the large ionisation disappears when oxygen is fed in so as to destroy the afterglow. As before, this is not a mere dilution effect, since the afterglow, and the ionisation with it, reappear when an equal stream of (inert) nitrogen is substituted for the oxygen tributary.

The galvanometer deflection is increased several fold if sodium vapour is introduced into the nitrogen between the testing electrodes, so as to develop the sodium spectrum.

Mercury vapour, introduced into the glowing nitrogen, did not much alter the conductivity of the latter, though its spectrum was completely replaced by the line spectrum of mercury.

Acetylene under the same conditions diminished the conductivity about three times. The cyanogen spectrum was alone visible in the region between the electrodes. For comparison of conductivities it was replaced by an equal stream of diluent nitrogen.

The chief point of interest brought out by these last experiments is that there is not always a much higher conductivity associated with the development of a line spectrum than with the development of a band spectrum. The spectra do not appear to be due to the recombination of ions. This was tested to some extent in the case of glowing nitrogen itself in the former paper.* An improved experiment has been carried out as follows: In order to make the most of the available voltage (200 volts) it was applied to a condenser with plates only 0·7 mm. apart. The glowing gas flowed between these plates along a length of 4 cm., and its luminosity could be observed by looking edgewise between them. A key was arranged so as to connect the plates together when up, and to connect them to the 200-volt supply when depressed. The luminosity was unaltered in intensity on depressing the key, whether the glow between the plates was that due to active nitrogen alone, or to acetylene or iodine stimulated by it. These spectra are therefore unaffected when a field of about 3000 volts per centimetre is applied to remove the ions.

The above condenser was not suitable to experiments with mercury vapour, as it was apt to be short-circuited by drops of condensed mercury. In this case I contented myself with passing the glow through a field of 100 volts per centimetre. No effect was observed.

* P. 221.

5. *Development of Metallic Spectra—Analogy with Ozone.*

I have seen no reason to modify the opinion before expressed that metallic line spectra developed in the afterglow are to be regarded as due to the combustion of the metal in active nitrogen. This opinion is supported in several cases by independent evidence that nitrogen is absorbed and a compound formed.

I have succeeded in observing analogous phenomena when metallic vapours are brought into contact with ozone. A current of oxygen was passed through a vacuum tube at low pressure, and a fragment of thallium heated to perhaps 300° C. in the issuing ozone. A spontaneous combustion of thallium vapour in ozone was observed with production of green thallium light. This at once ceased when the ozonising discharge was stopped. A similar combustion was obtained with sodium vapour, showing the D line only, without the green line so conspicuous when active nitrogen is used. No spectrum was observed with mercury. These phenomena are inconspicuous compared with those given by nitrogen. They are often interfered with by oxidation of the metallic surface, which hinders free evolution of vapour. I have not been tempted to study them in more detail.

6. *Attempts at Condensation.*

All attempts to isolate the active nitrogen by liquid air condensation have failed.

A closed vacuum tube, containing pure nitrogen, was partly immersed in liquid air, and the jar discharge passed for a considerable time. The afterglow was well developed, diffusing into those portions of the tube out of the direct line of discharge. No change of pressure could be observed, such as would be expected if any condensation of active nitrogen occurred. A tube charged with oxygen quickly runs "hard" under similar conditions, owing to the condensation of ozone.

These observations seem very unfavourable to the idea that active nitrogen has a complex atomic grouping, and, as far as they go, favourable to the idea before suggested, that it is monatomic. The simplicity of its spectrum in the visual region as compared with the ordinary nitrogen spectrum may be thought to point in the same direction.

7. *Summary.*

(1) Oxygen destroys active nitrogen, but does not combine with it. Hydrogen has no action.

(2) Active nitrogen, in reacting with nitric oxide to form the peroxide,

gives the same greenish-yellow flame with continuous spectrum which may be obtained by stimulating oxides of nitrogen in other ways.

(3) The reaction just mentioned is used to determine the percentage of active nitrogen present in ordinary nitrogen as it leaves the discharge. The result found is about 2·5 per cent., much higher than was formerly supposed.

(4) When dilute phosphorus vapour is introduced into glowing nitrogen it does not react at once. It is not until some time after the glow has completely disappeared that the nitrogen gets into a state in which it can react with phosphorus.

(5) The glow has a large electrical conductivity, comparable with that of a salted Bunsen flame. The ions are liberated in the glow, not merely carried forward from the original discharge. This ionisation is, as a rule, not very greatly affected when the spectra of other substances, such as metals or cyanogen, are developed by the active nitrogen in the space between the testing electrodes.

(6) None of these spectra are visibly diminished in intensity when large electromotive forces are applied to remove the ions.

(7) Ozone can in some cases develop metallic spectra when mixed at comparatively low temperatures with the metallic vapour.